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ORIGINAL PAPER

# Tartrate- and imidazole-derived diketones and diols: preparation and stability constants of their $Cu^{2+}$ complexes

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**Abstract** Overall, six tartrate- and imidazole-derived ketones and diols were synthesized in a stepwise manner as model compounds for the coordination of $Cu^{2+}$ ions. The stability constants of copper(II) complexes were studied spectrophotometrically. It was found that the two model structures coordinate $Cu^{2+}$ ions differentially.

**Keywords** Heterocycles · Ligands · Stability constant · Metal complexes · UV/vis spectroscopy

## Introduction

Tartaric acid and its functional derivatives represent a readily available, inexpensive, and optically active $C_2$-symmetric backbone [1]. Both (−)-(*S*,*S*)- and (+)-(*R*,*R*)-tartaric acid derivatives have found application in various areas of chemistry, such as: (i) the synthesis of chiral ligands and auxiliaries—chiral pool [2]; (ii) bioactive compounds [3]; (iii) resolution and fermentation processes [4]; (iv) chiral derivatizing agents for NMR [5]; (v) food additives [6]. Hence, tartaric acid derivatives have proven to be among the most pervasive and versatile precursors for the stereoselective elaboration and the construction of optically pure privileged ligands, such as α,α,α′,α′,-**t**etra-**a**ryl-1,3-**d**ioxolan-4,5-**d**imethan**ol**s (TADDOLs) and their modifications [7–9] (Fig. 1).

The first parent TADDOL derivative (Ar = Ph, R = $CH_3$) has been synthesized by Frankland [10] as early as 1904. However, the modern renaissance and the original name of TADDOL derivatives are ascribed to Seebach and co-workers [11, 12]. Since then, TADDOL derivatives evolved into easily accessible chiral ligands coordinating various (transition) metals and, especially the titanium TADDOL complexes, found applications in a variety of reactions [13].

Within the course of our research focused on the development of new optically active imidazole derivatives and their application as ligands chelating mainly $Cu^{2+}$ ions, we have synthesized several α-amino acid- [14–19] and terpene-derived [20, 21] imidazoles. Hence, we report herein a new family of imidazole-derived diketones and diols featuring the tartaric acid motive and investigation of their $Cu^{2+}$ complexes.

## Results and discussion

### *Synthesis*

Our synthesis started with the preparation of dimethyl (4*R*,5*R*)-2,2-dimethyl-1,3-dioxolan-4,5-dicarboxylate (**1**). Dicarboxylate **1** was easily generated from the commercially available (*R*,*R*)-tartaric acid by the reaction with 2,2-dimethoxypropane and *p*-toluenesulfonic acid [22]. Three basic imidazole derivatives, namely, 1-methylimidazole (**2**) [23], 1,4,5-trimethylimidazole (**3**) [24], and 1-methyl-4,5-diphenylimidazole (**4**) [23, 25], were chosen as the starting heterocycles. The first attempted nucleophilic additions of C2-lithiated imidazoles **2**–**4** to dicarboxylate **1** proved to be difficult due to the unselective formation of several badly separable products. Hence, we turned our attention towards (4*R*,5*R*)-*N*,*N*,*N*′,*N*′,2,2-hexamethyl-1,3-dioxolan-4,5-dicarboxamide (**5**), which undergoes the desired nucleophilic

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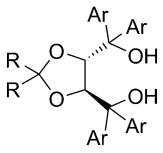
**Fig. 1** The TADDOL structure

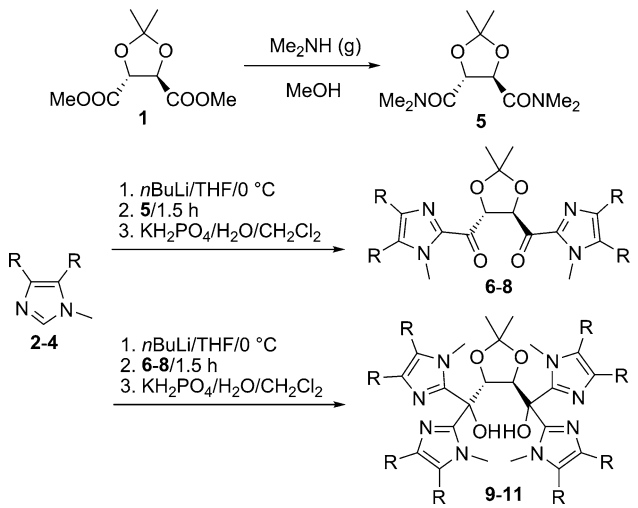


substitution more selectively [26]. Thus, the reaction of dicarboxylate **1** with dimethylamine afforded smoothly dicarboxamide **5** [27, 28]. Selective C2-lithiation of imidazoles **2–4** and subsequent addition of the organolithium intermediates to dicarboxamide **5** afforded the desired diketones **6–8**. However, the reaction conditions needed to be optimized. We found that the highest yields and purity of the desired diketones **6–8** can be achieved under the following conditions: ratio of the lithiated imidazole and the carboxamide 4:1, reaction temperature 0 °C, and reaction time of 1.5 h followed by the reaction quench with aqueous phosphate buffer should be used. Under these conditions, diketones **6–8** were isolated in 54–83% yields (Scheme 1, Table 1).

Diketones **6–8** were in the next reaction step repeatedly treated with the C2-lithiated imidazoles **2–4** under the aforementioned conditions to afford target diols **9–11** in yields of 48–67% (Scheme 1, Table 1). It should be noted that direct fourfold addition of the C2-lithiated imidazoles **2–4** to dicarboxamide **5** yielded a mixture of several inseparable products and, therefore, the stepwise addition was necessary.

*Complexation*

The formation of coordination compounds between metal ions M and ligand L in the solution can be described by the following reaction:




**Scheme 1**

**Table 1** Structure, yields, melting points, and optical rotations of the synthesized diketones **6–8** and diols **9–11**

| Comp. | R | Yield/% | m.p./°C | $[\alpha]_D^{20a}$/deg cm$^2$ g$^{-1}$ |
|---|---|---|---|---|
| **6** | H | 58 | 96–97 | −180.8 |
| **7** | Me | 54 | 85–86 | −130.3 |
| **8** | Ph | 83 | 110–111 | +134.0 |
| **9** | H | 67 | 204–205 | −206.8 |
| **10** | Me | 66 | 139–140 | −143.6 |
| **11** | Ph | 48 | 197–198 | −85.6 |

[a] Concentration $c$ is 0.5 g/100 cm$^3$ MeOH

$$m\mathrm{M} + n\mathrm{L} \rightleftarrows \mathrm{M_mL_n}$$

where $m$ is the number of metal ions and $n$ means the number of ligand molecules in the complex $M_mL_n$. The particular equilibrium is described by the stability constant of the complex defined by equation Eq. 1:

$$\beta_{mn} = \frac{\lfloor \mathrm{M_mL_n} \rfloor}{[\mathrm{M}]^m \mathrm{x} [\mathrm{L}]^n} \quad (1)$$

where $\beta_{mn}$ is the stability constant of the complex $M_mL_n$. Spectrophotometric titration is a common technique used for the determination of the stability constants $\beta_{mn}$. Thus, spectrophotometric titration of ligands **6–11** and $Cu^{2+}$ ions in methanol has been employed to determine the stability constants $\beta_{mn}$ (Fig. 2). Factor analysis of the matrix of absorbancies (see "Experimental") during titration indicated approximately 4–5 species with different absorption spectra. This implies that, in the solution, two or three complexes are being formed. The detailed analysis through the EFA profiles [29, 30] modified for the factor analysis

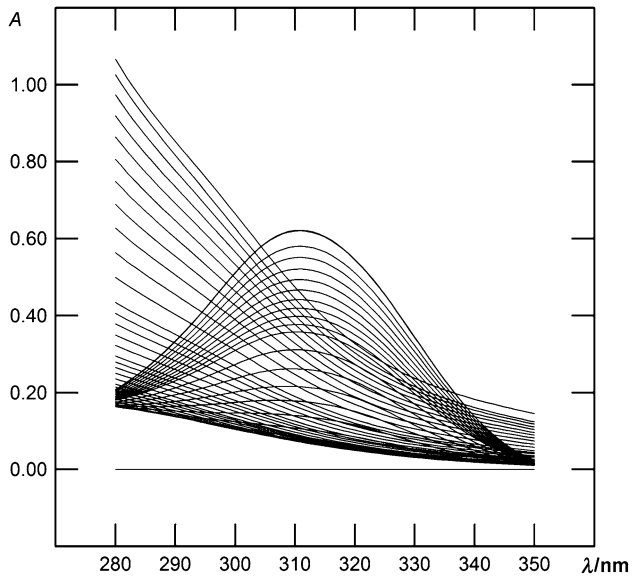



**Fig. 2** The change in the UV/vis spectra of the ligand **7** in methanol as a function of the copper(II) acetate addition during the titration

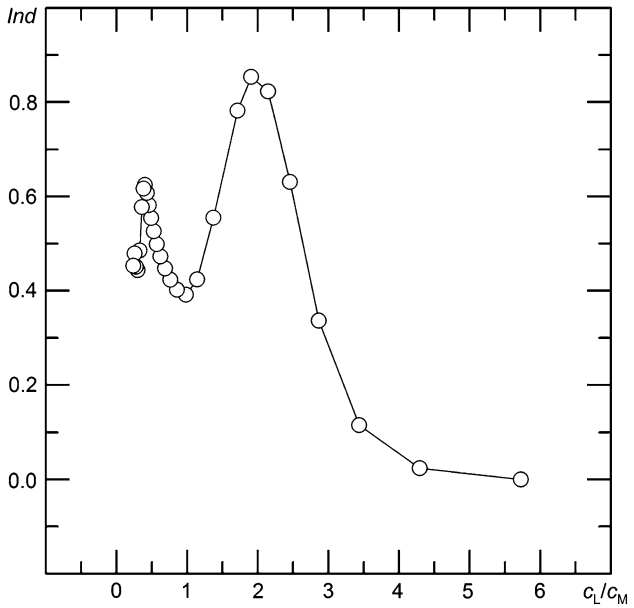



**Fig. 3** The indication of the ratio of metal:ligand (2:1 and 1:2) in the $Cu^{2+}$ complexes with **11** in dependence on the ratio of the analytical concentrations of ligand $c_L$ and metal ions $c_M$

[29] revealed that, whereas diketones **6–8** form 2:1, 1:1, and 1:2 complexes (metal:ligand) with $Cu^{2+}$ ions, diols **9–11** give only 2:1 and 1:2 complexes. A representative output of such analysis for ligand **11** is shown in Fig. 3. This observation was also verified by the calculation of various models comprising different types of complexes. The calculation using the general model, which comprises the formation of $M_2L$, ML, and $ML_2$ complexes, provided the corresponding stability constants of ketones **6–8**. In the case of diols **9–11**, the stability constant $\beta_{11}$ was statistically not significant and, therefore, a simplified model comprising only the formation of $M_2L$ and $ML_2$ complexes was used. The stability constant values for compounds **6–11** and $Cu^{2+}$ ions in methanol are summarized in Table 2.

The data in Table 2 show that the stability constants $\beta_{21}$ and $\beta_{11}$ for diketones **6–8** in dependence on the imidazole C4/C5 substitution differ only slightly. The highest value of $\beta_{21}$ was obtained for the phenyl-disubstituted diketone **8**, which is most probably given by the sterically hindered coordination of the acetate anions or molecules of solvent as coligands to the two coordinated $Cu^{2+}$ ions. Hence, the $Cu^{2+}$ ions were coordinated by ligand **8** in the most efficient way. The formation of a 1:1 complex apparently requires sterically more hindered coordination of both imidazole rings. The appended substituents at imidazole positions C4/C5 in ketones **7** and **8** hinder the access of $Cu^{2+}$ ions and, therefore, the stability constants $\beta_{11}$ are generally smaller. However, the imidazole C4/C5 substitution influences the stability constants $\beta_{12}$ more dramatically. The unsubstituted derivative **6** forms a stable complex with two ligands coordinated to one $Cu^{2+}$ ion. In contrast to this, the coordination of two ligands **8** with bulky and rigid phenyl substituents is considerably hindered and, therefore, the stability constant $\beta_{12}$ is almost negligible for ligand **8**. From these relationships, we can deduce that the coordination sites for $Cu^{2+}$ ions in diketones **6–8** are most probably the carbonyl oxygens or the imidazole nitrogens.

In comparison to diketones **6–8**, the absence of an ML complex for alcohols **9–11** reflects a different structure of the coordination site. It seems that diketones **6–8** coordinate $Cu^{2+}$ ions in ML complexes via carbonyl oxygens and less through the imidazole nitrogen N3. However, a cumulation of bulky groups that hinder efficient coordination in the ML type of complexes can be the second explanation. The relationship of the stability constants $\beta_{21}$ ($M_2L$) in dependence on the imidazole C4/C5 substitution is similar to for diketones **6–8**. This implies that the same coordination site is employed in both types of compounds, most probably imidazole N3. A weak dependence of the stability constant $\beta_{12}$ on the imidazole C4/C5 substitution reveals that imidazole N3 is not a coordination site in the $ML_2$ complexes of diols **9–11**. A coordination of two ligands through four hydroxy groups seems to be more probable. A small increase of the stability constant $\beta_{12}$ as a consequence of imidazole C4/C5 substituents can be related to the sterically hindered coordination of the acetate anions or the molecules of solvent as coligands.

**Table 2** The calculated stability constants $\beta$ for diketones **6–8** and diols **9–11**, their standard deviations, and residual standard deviations of the nonlinear regression $s$

| Comp. | R | log $\beta_{21}$ ($M_2L$) | log $\beta_{11}$ (ML) | log $\beta_{12}$ ($ML_2$) | $s$ |
|---|---|---|---|---|---|
| **6** | H | 10.29 ± 0.010 | 7.100 ± 0.010 | 12.76 ± 0.009 | $1.08 \times 10^{-3}$ |
| **7** | Me | 10.03 ± 0.013 | 5.991 ± 0.005 | 9.587 ± 0.001 | $6.89 \times 10^{-3}$ |
| **8** | Ph | 11.38 ± 0.042 | 6.164 ± 0.036 | 3.302 ± 0.086 | $4.24 \times 10^{-3}$ |
| **9** | H | 7.323 ± 0.001 | [a] | 9.014 ± 0.001 | $2.89 \times 10^{-3}$ |
| **10** | Me | 6.888 ± 0.004 | [a] | 9.534 ± 0.006 | $5.51 \times 10^{-3}$ |
| **11** | Ph | 8.449 ± 0.003 | [a] | 10.13 ± 0.01 | $5.67 \times 10^{-3}$ |

[a] This type of complex was not observed

## Conclusion

Starting from dicarboxamide **5**, diketones **6–8** and diols **9–11** were prepared by the nucleophilic addition of C2-lithiated imidazole species. The direct fourfold addition proved to be difficult and, therefore, the stepwise addition was necessary. Both diketones **6–8** and TADDOL-like diols **9–11** were examined as model compounds for the complexation of $Cu^{2+}$ ions. Whereas diketones **6–8** formed the expected $M_2L$, ML, and $ML_2$ complex species, diols **9–11** provided only $M_2L$ and $ML_2$ types of complexes.

## Experimental

The reagents and solvents were reagent-grade and were purchased from Penta, Aldrich, and Acros, and used as received. The starting dicarboxylate **1** [22], imidazoles **2–4** [23–25], and dicarboxamide **5** [27, 28] were synthesized according to literature procedures. All reactions were performed in flame-dried flasks under inert argon atmosphere. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl radical. Column chromatography was carried out with silica gel 60 (particle size 0.040–0.063 mm, 230–400 mesh; Merck) and commercially available solvents. Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with silica gel 60 $F_{254}$ obtained from Merck, with visualization by UV lamp (254 or 360 nm). $^1$H and $^{13}$C NMR spectra were recorded at 400 and 100 MHz, respectively, with a Bruker Avance 400 instrument at 25 °C. Chemical shifts are reported in ppm relative to the signal of $Me_4Si$. The residual solvent signal in the $^1$H and $^{13}$C NMR spectra was used as an internal reference ($CDCl_3$—7.25 and 77.23 ppm). Apparent resonance multiplicities are described as s (singlet), br s (broad singlet), d (doublet), and m (multiplet). Mass spectra were measured on a GC/MS configuration comprised of an Agilent Technologies 6890N gas chromatograph equipped with a 5973 Network MS detector (EI 70 eV, mass range 33–550 Da) or on an LC–MS Micromass Quattro Micro API (Waters) instrument with a direct input (ESI+ , $CH_3OH$, mass range 200–800 Da). IR spectra were recorded on a Perkin Elmer FT-IR Spectrum BX spectrometer. Optical rotations were measured on a Perkin Elmer 341 polarimeter using the sodium D line (589 nm), specific rotations [α] are given in units of deg cm$^2$ g$^{-1}$, and concentration $c$ is 0.5 g/100 cm$^3$ MeOH. Elemental analyses were performed on an EA 1108 Fisons instrument, and their results were found to be in good agreement with the calculated values.

*General procedure for the synthesis of diketones **6–8***

To imidazole **2–4** (16.0 mmol) dissolved in 50 cm$^3$ THF, 10.25 cm$^3$ of *n*BuLi (16.4 mmol, 1.6 M solution in hexane) was added at 0 °C under argon. The yellow or orange reaction mixture was stirred for 15 min, whereupon 0.98 g of **5** (4.0 mmol) dissolved in 30 cm$^3$ THF was added. The reaction mixture was stirred for 1.5 h at 0 °C and poured into a vigorously stirred biphasic system of 200 cm$^3$ aqueous $KH_2PO_4$ (10%) and 200 cm$^3$ $CH_2Cl_2$. The organic phase was separated, the aqueous layer was extracted with 2 × 150 cm$^3$ $CH_2Cl_2$, the combined organic layers were dried ($Na_2SO_4$), and the solvents were evaporated at reduced pressure. The resulting crude product was purified on column chromatography using the indicated solvent system.

*[(4R,5R)-2,2-dimethyl-1,3-dioxolane-4,5-diyl]bis-[(1-methyl-1H-imidazol-2-yl)methanone]*
(**6**, $C_{15}H_{18}N_4O_4$)
Off-white solid. Yield 0.74 g (58%); m.p.: 96–97 °C; $R_f = 0.38$ ($SiO_2$; EtOAc); $[\alpha]_D^{20} = -180.8°$ cm$^2$ g$^{-1}$ ($c = 0.5$, MeOH); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.54$ (s, 6H, 2 × $CH_3$), 4.00 (s, 6H, 2 × $NCH_3$), 5.87 (s, 2H, 2 × CH), 6.84 (s, 2H, 2 × $CH_{im}$), 6.94 (s, 2H, 2 × $CH_{im}$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 26.78$, 35.95, 79.17, 113.33, 127.21, 129.60, 142.09, 186.63 ppm; IR (neat): $\bar{\nu} = 3{,}132$, 2,985, 2,926, 1,682 (C=O), 1,403, 1,260, 1,206, 1,160, 1,043, 978, 881, 862, 780, 754, 700 cm$^{-1}$; EI-MS (70 eV): $m/z = 318$ ($M^+$, 1), 260 (24), 209 (61), 181 (57), 151 (100), 109 (94).

*[(4R,5R)-2,2-dimethyl-1,3-dioxolane-4,5-diyl]bis[(1,4,5-trimethyl-1H-imidazol-2-yl)methanone]*
(**7**, $C_{19}H_{26}N_4O_4$)
Off-white solid. Yield 0.81 g (54%); m.p.: 85–86 °C; $R_f = 0.49$ ($SiO_2$; EtOAc); $[\alpha]_D^{20} = -130.3°$ cm$^2$ g$^{-1}$ ($c = 0.5$, MeOH); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.55$ (s, 6H, 2 × $CH_3$), 1.85 (s, 6H, 2 × $C_{im}CH_3$), 2.09 (s, 6H, 2 × $C_{im}CH_3$), 3.89 (s, 6H, 2 × $NCH_3$), 5.78 (s, 2H, 2 × CH) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 8.93$, 12.69, 26.77, 32.72, 79.39, 112.82, 130.93, 136.03, 140.38, 185.92 ppm; IR (neat): $\bar{\nu} = 3{,}434$, 2,983, 2,921, 1,669 (C=O), 1,560, 1,463, 1,373, 1,293, 1,180, 1,104, 1,013, 942, 900, 779, 727 cm$^{-1}$; EI-MS (70 eV): $m/z = 374$ ($M^+$, 2), 316 (27), 237 (19), 179 (100), 137 (99), 110 (22), 56 (23).

*[(4R,5R)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis-[(1-methyl-4,5-diphenyl-1H-imidazol-2-yl)methanone]*
(**8**, $C_{39}H_{34}N_4O_4$)
Off-white solid. Yield 2.07 g (83%); m.p.: 110–111 °C; $R_f = 0.63$ ($SiO_2$; EtOAc/hexane 1:1); $[\alpha]_D^{20} = +134.0°$ cm$^2$ g$^{-1}$ ($c = 0.5$, MeOH); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.73$ (s, 6H, 2 × $CH_3$), 3.62 (s, 6H, 2 × $NCH_3$), 6.14 (s, 2H, 2 × CH), 6.70 (d, 4H, $J = 7.2$ Hz, Ph), 7.11–7.14 (m, 6H, Ph), 7.24–7.30 (m, 8H, Ph), 7.35–7.39 (m, 2H, Ph) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 26.89$, 33.53, 79.93,

112.90, 126.45, 127.20, 128.29, 129.15, 129.27, 129.45, 130.49, 133.33, 135.33, 138.27, 141.36, 186.50 ppm; IR (neat): $\bar{\nu}$ = 3,053, 2,985, 2,934, 1,684 (C=O), 1,446, 1,379, 1,202, 1,112, 1,025, 989, 954, 902, 770, 694 $cm^{-1}$; EI-MS (70 eV): *m/z* = 234 (100), 218 (14), 165 (48); ESI–MS: *m/z* = 623 $(M + 1)^+$, 645 $(M + 23)^+$, 1,267 $(2M + 23)^+$.

*General procedure for the synthesis of diols* ***9–11***

To imidazole **2–4** (2.0 mmol) dissolved in 20 $cm^3$ THF, 1.28 $cm^3$ of *n*BuLi (2.05 mmol, 1.6 M solution in hexane) was added at 0 °C under argon. The yellow or orange reaction mixture was stirred for 15 min, whereupon diketone **6–8** (0.5 mmol) dissolved in 15 $cm^3$ THF was added. The reaction mixture was stirred for 1.5 h at 0 °C and poured into a vigorously stirred biphasic system of 50 $cm^3$ aqueous $KH_2PO_4$ (10%) and 50 $cm^3$ $CH_2Cl_2$. The organic phase was separated, the aqueous layer was extracted with 2 × 50 $cm^3$ $CH_2Cl_2$, the combined organic layers were dried ($Na_2SO_4$), and the solvents were evaporated at reduced pressure. The resulting crude product was purified on column chromatography using the indicated solvent system.

*[(4R,5R)-2,2-dimethyl-1,3-dioxolane-4,5-diyl]bis[bis(1-methyl-1H-imidazol-2-yl)methanol]* (***9***, $C_{23}H_{30}N_8O_4$)
Off-white solid. Yield 161 mg (67%); m.p.: 204–205 °C; $R_f$ = 0.25 ($SiO_2$; EtOAc/MeOH 5:1); $[\alpha]_D^{20}$ = −206.8° $cm^2$ $g^{-1}$ (*c* = 0.5, MeOH); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.32 (s, 6H, 2 × $CH_3$), 3.24 (s, 6H, 2 × $NCH_3$), 3.98 (s, 6H, 2 × $NCH_3$), 5.33 (s, 2H, 2 × CH), 6.47 (s, 4H, 4 × $CH_{im}$), 6.77 (s, 2H, 2 × $CH_{im}$), 6.82 (s, 2H, 2 × $CH_{im}$), 9.26 (br s, 2H, OH) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 26.79, 33.93, 35.62, 73.74, 81.21, 106.27, 122.35, 122.54, 123.69, 126.92, 146.78, 149.03 ppm; IR (neat): $\bar{\nu}$ = 2,981 (OH), 1,461, 1,388, 1,280, 1,239, 1,118, 1,070, 985, 896, 728, 717, 685 $cm^{-1}$; ESI–MS: *m/z* = 505 $(M + 23)^+$, 987 $(2M + 23)^+$.

*[(4R,5R)-2,2-dimethyl-1,3-dioxolane-4,5-diyl]bis-[bis(1,4,5-trimethyl-1H-imidazol-2-yl)methanol]*
(**10**, $C_{31}H_{46}N_8O_4$)
Off-white solid. Yield 196 mg (66%); m.p.: 139–140 °C; $R_f$ = 0.30 ($SiO_2$; EtOAc/MeOH 5:1); $[\alpha]_D^{20}$ = −143.6° $cm^2$ $g^{-1}$ (*c* = 0.5, MeOH); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.35 (s, 6H, 2 × $CH_3$), 1.81 (s, 6H, 2 × $C_{im}CH_3$), 1.89 (s, 6H, 2 × $C_{im}CH_3$), 2.04 (s, 6H, 2 × $C_{im}CH_3$), 2.12 (s, 6H, 2 × $C_{im}CH_3$), 3.10 (s, 6H, 2 × $NCH_3$), 3.84 (s, 6H, 2 × $NCH_3$), 5.26 (s, 2H, 2 × CH), 9.53 (br s, 2H, OH) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 8.62, 9.35, 11.92, 13.03, 26.97, 31.20, 33.08, 73.77, 81.58, 105.99, 123.15, 123.77, 128.20, 131.13, 144.98, 147.24 ppm; IR (neat): $\bar{\nu}$ = 2,918 (OH), 1,721, 1,440, 1,396, 1,369, 1,222, 1,128, 1,069, 1,004, 911, 870, 781, 698 $cm^{-1}$; ESI–MS: *m/z* = 595 $(M + 1)^+$, 1211 $(2M + 23)^+$.

*[(4R,5R)-2,2-dimethyl-1,3-dioxolane-4,5-diyl]bis-[bis(1-methyl-4,5-diphenyl-1H-imidazol-2-yl)methanol]*
(**11**, $C_{71}H_{62}N_8O_4$)
Off-white solid. Yield 262 mg (48%); m.p.: 197–198 °C; $R_f$ = 0.63 ($SiO_2$; EtOAc/hexane 1:2); $[\alpha]_D^{20}$ = −85.6° $cm^2$ $g^{-1}$ (*c* = 0.5, MeOH); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.59 (s, 6H, 2 × $CH_3$), 2.73 (s, 6H, 2 × $NCH_3$), 3.93 (s, 6H, 2 × $NCH_3$), 5.86 (s, 2H, 2 × CH), 7.05–7.53 (m, 40H, Ph), 9.60 (br s, 2H, OH) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 27.13, 31.84, 34.10, 74.59, 81.58, 106.69, 125.85, 126.25, 126.54, 126.66, 127.99, 128.14, 128.52, 128.59, 128.89, 128.94, 130.24, 130.46, 130.96, 131.10, 131.43, 131.83, 133.26, 134.03, 135.24, 135.76, 146.44, 149.28 ppm; IR (neat): $\bar{\nu}$ = 2,887 (OH), 1,600, 1,504, 1,441, 1,370, 1,230, 1,133, 1,053, 1,024, 908, 771, 693 $cm^{-1}$; ESI–MS: *m/z* = 1,113 $(M + 23)^+$.

*Stability constant β determination*

The stability constants of the complexes prepared from ligands **6–11** and $Cu^{2+}$ ions were determined by spectrophotometric titration at 25 °C. A 1-cm-wide quartz cuvette was filled with 3 $cm^3$ of ligand solution in methanol ($c = 2 \times 10^{-5}$ mol/$dm^3$) and the absorption spectrum was measured in the range of wavelengths $\lambda$ from 280 to 350 nm. A 745 $mm^3$ quantity of solution of copper(II) acetate in methanol ($c = 2 \times 10^{-3}$ mol/$dm^3$, the accurate concentration was determined by ICP) was added gradually in 2–50-$mm^3$ portions. The additions were optimized with respect to the molar ratio of ligand:metal (15:1 at the beginning, 1:25 at the end, 45 additions overall). The absorption spectra were recorded upon each $Cu^{2+}$ addition. The absorption spectrum of 745 $mm^3$ of the aforementioned copper(II)acetate solution in 3 $cm^3$ of methanol was measured at the end. The stability constants $\beta$ and their molar absorption coefficients $\varepsilon$ ($\lambda$) were calculated from the matrix of measured absorbancies (row—concentrations, columns—wavelengths) employing the program OPchem [31]. The same program was used for the determination of the number of particles in the solution and for the indication of the complexes with the given ratio of metal:ligand.

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